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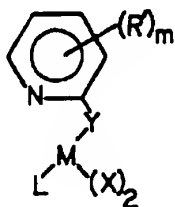
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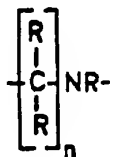
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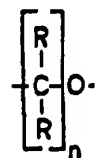
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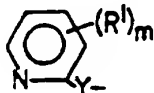
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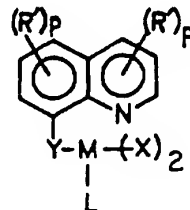
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(57) Abstract

Disclosed is a novel bidentate pyridine transition metal catalyst having general formula (1), where Y is O, S, NR, (2), or (3), each R is independently selected from hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl, each R' is independently selected from C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>1</sub> to C<sub>6</sub> alkoxy, C<sub>6</sub> to C<sub>16</sub> aryl, halogen, or CF<sub>3</sub>, M is titanium, zirconium, or hafnium, each X is independently selected from halogen, C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>1</sub> to C<sub>6</sub> alkoxy, or (4), L is X, cyclopentadienyl, C<sub>1</sub> to C<sub>6</sub> alkyl substituted cyclopentadienyl, indenyl, fluorenyl, or (5), "m" is 0 to 4, and "n" is 1 to 4. Also disclosed is a method of making a poly-α-olefin comprising polymerizing an α-olefin monomer using that catalyst or a catalyst that has general formula (6), where Y, M, L, X, and R' were previously defined and each "p" is independently selected from 0 to 3.

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TRANSITION METAL CATALYST BASED ON BIDENTATE LIGANDS CONTAINING PYRIDINE  
OR QUINOLINE MOIETY

Background of the Invention

5 This invention relates to catalysts useful in  
polymerizing  $\alpha$ -olefins. In particular, it relates to the  
polymerization of ethylene using transition metal catalysts  
with bidentate ligands containing pyridine or quinoline  
moieties.

10 Until recently, polyolefins have been made primarily  
using conventional Ziegler catalyst systems. A Ziegler  
catalyst typically consists of a transition metal-containing  
compound and one or more organometallic compounds. For  
example, polyethylene has been made using Ziegler catalysts  
such as titanium trichloride and diethylaluminum chloride, or  
15 a mixture of titanium tetrachloride, vanadium oxytrichloride,  
and triethylaluminum. These catalysts are inexpensive but  
they have low activity and therefore must be used at high  
concentrations. The catalyst residue in the polymers produce  
a yellow or grey color and poor ultraviolet and long term  
20 stability, and chloride-containing residues can cause  
corrosion in polymer processing equipment. It is therefore  
sometimes necessary to either remove catalyst residues from  
the polymer or add neutralizing agents and stabilizers to the

polymer to overcome the deleterious effects of the residues and this adds to production costs. Furthermore, Ziegler catalysts produce polymers having a broad molecular weight distribution, which is undesirable for some applications such as injection molding. They are also poor at incorporating  $\alpha$ -olefin co-monomers, making it difficult to control polymer density. Large quantities of excess co-monomer may be required to achieve a certain density and many higher  $\alpha$ -olefins, such as 1-octene, can be incorporated at only very low levels, if at all.

Although substantial improvements in Ziegler catalyst systems have occurred since their discovery, these catalysts are now being replaced with recently discovered metallocene catalyst systems. A metallocene catalyst typically consists of a transition metal compound that has one or more cyclopentadienyl ring ligands. Metallocenes have low activities when used with organometallic compounds, such as aluminum alkyls, which are used with traditional Ziegler catalysts, but very high activities when used with aluminoxanes as cocatalysts. The activities are generally so high that catalyst residues need not be removed from the polymer. Furthermore, they produce polymers with high molecular weights and narrow molecular weight distributions. They also incorporate  $\alpha$ -olefin co-monomers well.

However, at higher temperatures metallocene catalysts tend to produce lower molecular weight polymers. Thus, they are useful for gas phase and slurry polymerizations of ethylene, which are conducted at about 80°C to about 95°C, but in general they do not work well as temperatures are increased. The polymerization of ethylene in solution is desirable because it allows great flexibility for producing polymers over a wide range of molecular weights and densities as well as the use of a large variety of different co-monomers. Solution polymerization permits the production of polymers that are useful in many different applications. For example, both high molecular weight, high density polyethylene (PE) film useful as a barrier film for food packaging and low density ethylene co-polymers with good toughness and high impact strength can be made.

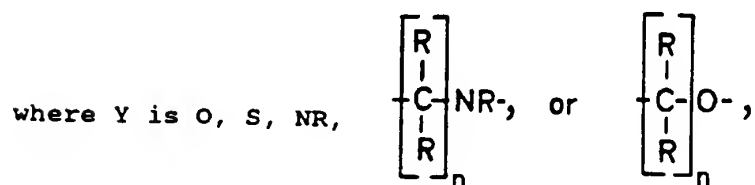
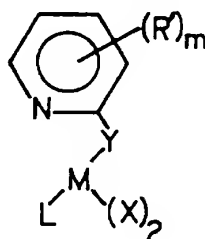
#### Summary of the Invention

We have discovered novel bidentate pyridine transition metal compounds which have excellent activity as  $\alpha$ -olefin polymerization catalysts. We have also discovered that bidentate quinoline transition metal compounds, which were heretofore unsuspected of possessing any catalytic properties, are also excellent polymerization catalysts for  $\alpha$ -olefins. These catalysts produce polymers having properties very close

to the properties of polymers produced using metallocene catalysts. That is, the polymers have a narrow molecular weight distribution and a uniform co-monomer incorporation.

#### Description of the Preferred Embodiments

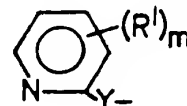
5           The transition metal catalysts of this invention containing the bidentate pyridine based ligand have the general formula



each R is independently selected from hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl, each R' is independently selected from C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>1</sub> to C<sub>6</sub> alkoxy, C<sub>6</sub> to C<sub>16</sub> aryl, halogen, or CF<sub>3</sub>, M is titanium, zirconium, or hafnium, each X is independently selected from halogen, C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>1</sub> to C<sub>6</sub> alkoxy, or



10           L is X, cyclopentadienyl, C<sub>1</sub> to C<sub>6</sub> alkyl substituted cyclopentadienyl, indenyl, fluorenyl, or



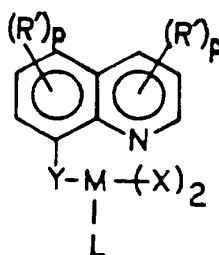
15           "m" is 0 to 4, and "n" is 1 to 4.

In the formula, the Y group is preferably oxygen as those compounds are easier to make. For the same reason the R group is preferably methyl and "m" is preferably 0. The L group is preferably halogen, most preferably chlorine, as those catalysts give superior properties and are easier to  
5 prepare. For the same reasons, the X group is preferably halogen, especially chlorine, and the M group is preferably titanium.

Preparation of the bidentate pyridine complexes is  
10 illustrated in the examples, but generally they can be prepared by reacting a substituted pyridine precursor having an acidic proton with a compound having the formula  $MX_3L$  in the presence of an HX scavenger. The reaction is stoichiometric and stoichiometric amounts of scavenger are  
15 preferred. Examples of suitable scavengers include compounds that are more basic than the substituted pyridine, such as triethylamine, pyridine, sodium hydride, and butyl lithium. If the scavenger is a stronger base than the substituted pyridine one can make a salt of the substituted pyridine and  
20 begin with that. While the reaction is preferably performed in a solvent, only partial solubility of the reactants is required. An aprotic solvent, such as tetrahydrofuran (THF), ether, toluene, or xylene, can be used at about 0.2 to about 20 wt% solids, and preferably at about 5 to about 10 wt%  
25 solids. The reaction can occur at about  $-78^{\circ}\text{C}$  to about room

temperature. As the reaction proceeds a precipitate is formed and the product can be extracted with toluene, methylene chloride, diethyl ether, or a similar extractant.

The bidentate quinoline transition metal catalysts of this invention have the general formula



where  $R$ ,  $R'$ ,  $L$ ,  $M$ ,  $X$ , and " $n$ " were previously defined and each " $p$ " is independently selected from 0 to 3.

The quinoline transition metal catalysts are made in a similar manner to the pyridine transition metal catalysts except that one begins with a substituted quinoline such as 8-hydroxy quinoline (also known as 8-quinolinol) instead of the substituted pyridine. Also, butyl lithium can be used in a solvent to make the lithium salt of 8-hydroxy quinoline, which can also be used as the starting material.

Since the catalyst is normally used in conjunction with an organometallic co-catalyst, it is preferable to dissolve

the catalyst in a solvent in which the co-catalyst is also soluble. For example, if methylaluminoxane (MAO) or polymethylaluminoxane (PMAO) is the co-catalyst then toluene, xylene, benzene, or ethylbenzene could be used as the solvent.

5 The preferred co-catalyst is MAO as it results in high activity and a polymer having a narrower molecular weight distribution. The mole ratio of the organometallic co-catalyst to catalyst when used in a polymerization is generally in the range 0.01:1 to 100,000:1, and preferably  
10 ranges from 1:1 to 10,000:1.

An alternative co-catalyst is an acid salt that contains a non-coordinating inert anion (see U.S. Patent No. 5,064,802). The acid salt is generally a non-nucleophilic compound that consists of bulky ligands attached to a boron or  
15 aluminum atom, such as lithium tetrakis(pentafluorophenyl) borate, lithium tetrakis(pentafluorophenyl)aluminate, anilinium tetrakis(pentafluorophenyl)borate, and mixtures thereof. The anion which results when these compounds react with the catalyst is believed to be weakly coordinated to the  
20 metal-containing cation. The mole ratio of acid salt to catalyst can range from about 0.01:1 to about 1000:1, but is preferably about 1:1 to 10:1. While there is no limitation on the method of preparing an active catalyst system from the catalyst and the acid salt, preferably they

are mixed in an inert solvent at temperatures in the range of about -78°C to about 150°C. They can also be mixed in the presence of monomer if desired. The acid salt can be used in combination with the organometallic cocatalysts described earlier.

The catalyst and co-catalyst can be used on a support such as silica gel, alumina, silica, magnesia, or titania, but supports are not preferred as they may leave contaminants in the polymer. However, a support may be required depending upon the process being utilized. For example, a support is generally needed in gas phase polymerization processes and slurry polymerization processes in order to control the particle size of the polymer being produced and in order to prevent fouling of the reactor walls. To use a support, the catalyst and co-catalyst are dissolved in the solvent and are precipitated onto the support material by, for example, evaporating the solvent. The co-catalyst can also be deposited on the support or it can be introduced into the reactor separately from the supported catalyst.

The catalyst is used in a conventional manner in the polymerization of olefinic hydrocarbon monomers. While unsaturated monomers such as styrene can be polymerized using the catalysts of this invention, it is particularly useful for polymerizing  $\alpha$ -olefins such as propylene, 1-butene, 1-hexene, 1-octene, and especially ethylene.

The catalyst is also useful in a conventional manner for copolymerizing mixtures of unsaturated monomers such as ethylene, propylene, 1-butene, 1-hexene, 1-octene, and the like; mixtures of ethylene and di-olefins such as 1,3-butadiene, 1,4-hexadiene, 1,5-hexadiene, and the like; and mixtures of ethylene and unsaturated comonomers such as norbornene, ethylidene norbornene, vinyl norbornene, norbornadiene, and the like.

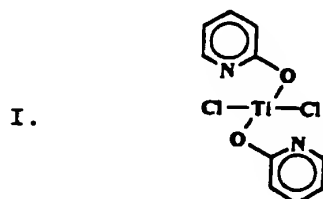
The catalysts of this invention can be utilized in a variety of different polymerization processes. They can be utilized in a liquid phase polymerization process (slurry, solution, suspension, bulk phase, or a combination of these), in a high pressure fluid phase, or in a gas phase polymerization process. The processes can be used in series or as individual single processes. The pressure in the polymerization reaction zones can range from about 15 psia to about 50,000 psia and the temperature can range from about -78°C to about 300°C.

#### EXAMPLE 1

##### Synthesis of Bis(2-pyridinoxy)titanium Dichloride

To a solution of 0.02 moles of 2-hydroxy pyridine and 0.02 moles of triethylamine in 50 mL of THF, a solution of 0.01 moles of titanium tetrachloride was added dropwise at 0°C

and stirred overnight at room temperature. After filtration, the THF solution was evaporated and the product was extracted from the residue. The product has the formula:

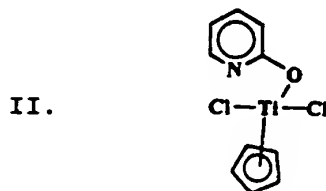


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#### EXAMPLE 2

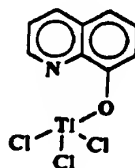
##### Preparation of (Cyclopentadienyl) (2-Pyridinoxy) Titanium Dichloride

To a solution of 0.002 moles of cyclopentadienyl titanium trichloride in 50 mL of ether a solution of 2-hydroxy pyridine (0.002 moles) and triethylamine (0.002 moles) in 50 mL of ether was added at 0°C and stirred overnight. The product was recovered from the ether filtrate. The product has the formula:



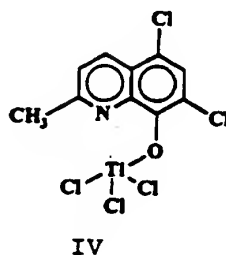
EXAMPLE 3General Procedure For Preparation  
of Quinolinoxyl Transition Metal Catalysts

5 Toluene slurries of lithium salts of various 8-quinolinol  
derivatives (prepared using butyl lithium) were combined with  
the corresponding titanium or zirconium compound (titanium  
tetrachloride, zirconium tetrachloride, cyclopentadienyl  
titanium trichloride, or cyclopentadienyl zirconium  
trichloride) at -78°C and stirred overnight at room  
10 temperature. The complexes were recovered from the reaction  
mixture by extraction with toluene or methylene chloride. To  
prepare 8-quinolinoxyl titanium trichloride (III),



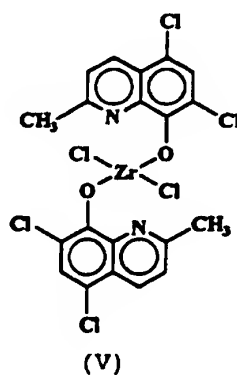
a slurry of 0.01 moles of the lithium salt of 8-  
hydroxyquinoline in 30 ml of toluene (prepared from 1.45 g  
15 (0.01 moles) of quinolinol and MeLi) was added at -78°C to a  
solution of 1.9 g (0.01 moles) of  $TiCl_4$  in 20 ml of toluene  
and stirred overnight at room temperature. The precipitate  
was separated, washed with toluene, and extracted with 100 ml  
of  $CH_2Cl_2$ . After the methylene chloride had been removed, a  
20 brown microcrystalline solid (0.7 g) was isolated.

Similarly, 8-(2-methyl-5,7-dichloroquinolin)oxytitanium trichloride (IV) (2.3 g)



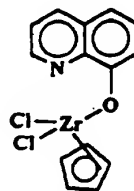
5 was prepared starting with a lithium salt made from 2.28 g (0.01 moles) of 5,7-dichloro-2-methyl-8-quinolinol.

A similar procedure was used to prepare 1.0 g of the comparative complex bis[8-(2-methyl-5,7-dichloroquinolin)oxy]zirconiumdichloride (V)



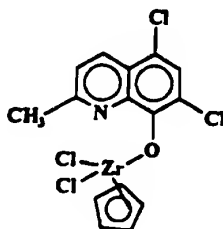
10 from 2.28 g (0.01 moles) of 5,7-dichloro-2-methyl-8-quinolinol and 1.165 g (0.005 moles) of zirconium tetrachloride .

To prepare (cyclopentadienyl)-(8-quinolinoxy)zirconium dichloride (VI)



(VI)

5 and (cyclopentadienyl)-[8-(2-methyl-5,7-dichloroquinolin)oxy]zirconium dichloride (VII)



(VII)

10 lithium salts made from 1.45 g (0.01 moles) of 8-quinolinol or 1.15 g (0.005 moles) of 5,7-dichloro-2-methyl-8-quinolinol, respectively, were reacted with equimolar amounts of cyclopentadienyl zirconium trichloride in toluene at -78°C. After stirring overnight and filtering, the products (0.62 g of VI and 1.7 g of VII) were isolated from the toluene solution.

EXAMPLE 4Polymerizations

5 All polymerizations in this study were conducted in a 1.7 L reactor. Prior to conducting a polymerization, the reactor was "baked-out" by heating to 130°C and holding at that temperature for 30 minutes under a nitrogen purge. Ethylene, hydrogen, hexene, butene, and nitrogen were treated by passage through columns containing 13X molecular sieves. For a typical polymerization, the reactor was charged with 10 0.850 L of hexane or toluene and, using a syringe, the required volume of diluted PMAO (AKZO). The desired amount of hydrogen was added to the reactor by monitoring the pressure drop ( $\Delta P$ ) from a 1 L stainless steel vessel pressurized with hydrogen. A toluene solution of catalyst was added to the 15 reactor by nitrogen over pressure. The reactor was maintained at isothermal conditions throughout the run. Ethylene was admitted to the reactor and controlled at 150 psi with feed on demand via a pressure regulator. After the reactor temperature and pressure stabilized, the catalyst slurry was 20 charged into the reactor and polymerization initiated. Ethylene flow was monitored via a Brooks mass flow meter.

Polymerization was terminated by venting the reactor and the polymer recovered by filtration. The polymer was stabilized by the addition of about 1000 ppm of butylated 25 hydroxytoluene/h xane (BHT) and further d volatilized 2 hours

at 80°C in a vacuum oven. Melt flow properties of the polymer were determined in accordance with ASTM D-1238. Polymer densities were measured on compression molded samples in a density gradient column in accordance with ASTM D-1505 85.

5           The following table gives the reaction conditions.

Run	Catalyst	Temp. (°C)	Co-Monomer	Co-Monomer (grams)	Catalyst (mmoles)	Molar Ratio Al/M	H <sub>2</sub> , ΔP	Reaction Time (Min)
1	I	80	None	0	9.5E-3	1897	0	15
2	I	80	None	0	4.7E-3	3795	0	15
3	I	80	None	0	4.7E-3	1897	20	15
4	I	80	None	0	4.7E-3	1897	50	10
5	I	80	Butene	20	4.7E-3	1897	20	15
6	II	80	None	0	9.0E-3	1001	0	60
7	III	80	Butene	10	8.4E-3	1074	10	30
8	III	80	None	10	8.4E-3	1074	10	30
9	IV	80	Butene	0	6.6E-3	1324	0	30
10	IV	80	Butene	10	6.6E-3	1324	10	30
11*	V	80	Butene	10	1.14E-2	1175	0	10
12*	V	80	Butene	10	4.06E-3	1645	0	10
13*	V	80	Butene	10	8.12E-3	1645	0	10
14	VI	80	Butene	10	6.74E-3	991	0	15
15	VI	80	Butene	10	1.35E-2	991	0	15
16	VI	80	Butene	10	1.35E-2	1288	5	15
17	VI	80	Butene	10	1.89E-2	1132	15	15
18	VI	110	Butene	10	1.89E-2	1132	0	15
19	VII	80	Butene	10	1.10E-2	1212	0	15
20	VII	80	Butene	10	1.10E-2	1212	5	15
21	VII	110	Butene	10	1.54E-2	1126	15	15
22	VII	80	Butene	10	1.54E-2	1126	0	15
23	VII	80	Butene	10	1.54E-2	2078	0	15

In the table, "Al/M" is ratio of moles of aluminum in PMAO to moles of metal (titanium or zirconium) in the catalyst.

\*Comparative Example

The following table gives the result of the polymerizations.

Run	Catalyst Productivity (kg/gM/h)	MI2	MI20	MFR	Density	Mw/Mn
1	179.0	<0.01	<0.01	-		
2	153.2	<0.01	<0.01	-		
3	165.5	<0.01	1.8	-		
4	133.1	<0.01	2.47	-		
5	272.9	<0.01	0.964	-		
6	62.9	<0.01	<0.01	-		
7	99.2	0.90	16.9	18.9	0.9513	2.51
8	167.9	0.41	4.2	10.2		3.67
9	103.2	<0.01	-	-		
10	24.8	<0.01	-	-		
11*	low	-	-	-		
12*	none	-	-	-		
13*	none	-	-	-		
14	none	-	-	-		
15	98.1	<0.01	1.15	-		
16	177.7	0.93	21.4	23.1		
17	137.6	1.31	34.5	26.3		
18	159.0	0.81	16.1	19.8		
19	119.8	<0.01	.83	-		
20	198.7	0.46	11.4	24.7		
21	157.8	0.63	17.8	28.2		
22	160.1	0.06	12.8	-		
23	112.1	0.06	1.84	29.7		

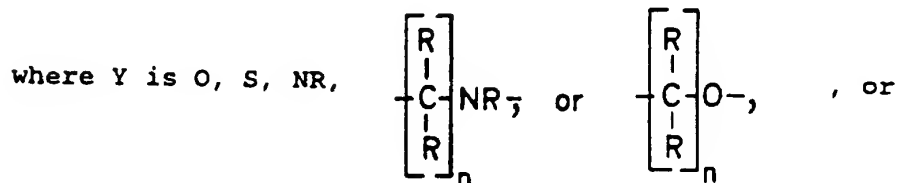
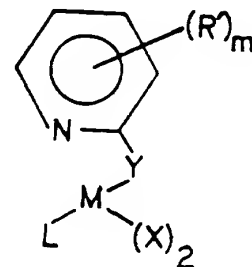
\*Comparative Example

In the table, kg/gm/h is kilograms polymer produced per gram of catalyst per hour. The melt index of the polymer was measured according to ASTM D-1238, Condition E and Condition F. MI2 is the melt index measured with a 2.16 kg weight (Condition E). MI20 is the melt index measured with a 21.6 kg weight (Condition F). MFR is the ratio of MI20 to MI2. The polymer density was measured according to ASTM D-1505. The molecular weight distribution of the polymer was measured using a Waters 150C gel permeation chromatograph at 135°C with 1,2,4-dichlorobenzene as the solvent. Both weight average molecular weight (Mw) and the ratio of Mw to Mn (number average molecular weight) are used to characterize the molecular weight distribution.

The catalysts of this invention gave good productivities and high molecular weight polymers, as evidenced by very low MI values, and Catalysts VI and VII did so even at higher temperatures (110°C).

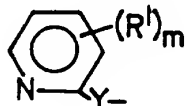
## WE CLAIM:

1. A catalyst having the general formula



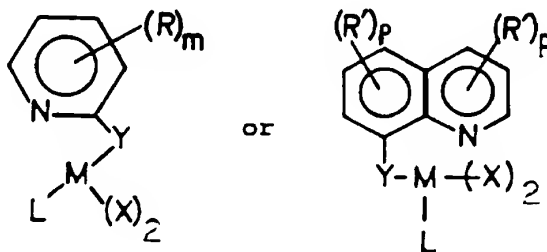
each R is independently selected from hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl, each R' is independently selected from C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>1</sub> to C<sub>6</sub> alkoxy, C<sub>6</sub> to C<sub>16</sub> aryl, halogen, or CF<sub>3</sub>, M is titanium, zirconium, or hafnium, each X is independently selected from halogen, C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>1</sub> to C<sub>6</sub> alkoxy, or  $\begin{array}{c} R \\ \diagup \\ -N \\ \diagdown \\ R \end{array}$ , L is X, cyclopentadienyl,

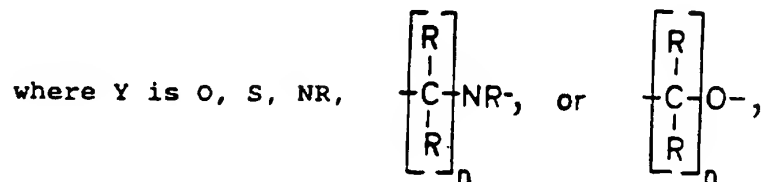
C<sub>1</sub> to C<sub>6</sub> alkyl substituted cyclopentadienyl, indenyl, fluorenyl or



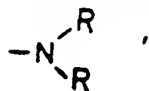
"m" is 0 to 4, and "n" is 1 to 4.

2. A catalyst according to Claim 1 wherein Y is oxygen.
3. A catalyst according to Claim 1 wherein X is halogen.
4. A catalyst according to Claim 3 wherein X is chlorine.
5. A catalyst according to Claim 1 wherein "m" is 0.
6. A catalyst according to Claim 1 wherein M is titanium.
7. A catalyst according to Claim 1 wherein M is zirconium.
8. A catalyst according to Claim 1 which is bis(2-pyridinoxy)titanium dichloride or (cyclopentadienyl(2-pyridinoxy)titanium dichloride.
9. A method of making a poly- $\alpha$ -olefin comprising polymerizing an  $\alpha$ -olefin monomer using a catalyst that has the general formula

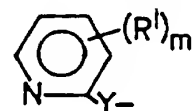




each R is independently selected from hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl, each R' is independently selected from R, C<sub>1</sub> to C<sub>6</sub> alkoxy, C<sub>6</sub> to C<sub>16</sub> aryl, halogen, or CF<sub>3</sub>, M is titanium, zirconium, or hafnium, each X is independently selected from halogen, C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>1</sub> to C<sub>6</sub> alkoxy, or

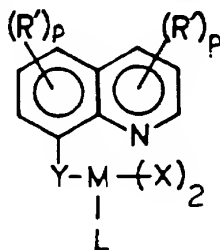


L is X, cyclopentadienyl, C<sub>1</sub> to C<sub>6</sub> alkyl substituted cyclopentadienyl, indenyl, fluorenyl, or



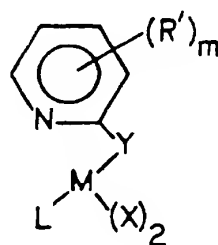
"m" is 0 to 4, and each "n" is 1 to 4, and each "p" is independently selected from 0 to 3.

10. A method according to Claim 9 wherein said catalyst has the general formula

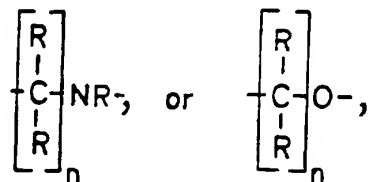


11. A method according to Claim 10 wherein Y is oxygen and X is halogen.
12. A method according to Claim 10 wherein M is titanium.
13. A method according to Claim 10 wherein M is zirconium.
14. A method according to Claim 13 wherein Y is oxygen and X is halogen.
15. A method according to Claim 14 wherein X is chlorine.
16. A method according to Claim 15 wherein L is cyclopentadienyl.
17. A method according to Claim 16 wherein R' is selected from the group consisting of chlorine, methyl, and mixtures thereof.
18. A method according to Claim 9 wherein said catalyst is selected from the group consisting of 8-quinolinoxy-titanium trichloride, 8-(2-methyl-5,7-dichloro-quinolin)oxytitanium trichloride, (cyclopentadienyl)-(8-quinolinoxy)zirconium dichloride, (cyclopentadienyl)-[8-(2-methyl-5,7-dichloroquinolin)oxy]zirconiumdichloride, and mixtures thereof.

19. A method of making a poly- $\alpha$ -olefin comprising polymerizing an  $\alpha$ -olefin monomer using a catalyst that has the general formula



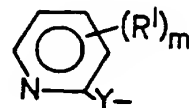
where Y is O, S, NR,



each R is independently selected from hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl, each R' is independently selected from C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>1</sub> to C<sub>6</sub> alkoxy, C<sub>6</sub> to C<sub>10</sub> aryl, halogen, or CF<sub>3</sub>, M is titanium, zirconium, or hafnium, each X is independently selected from halogen, C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>1</sub> to C<sub>6</sub> alkoxy, or



L is X, cyclopentadienyl, C<sub>1</sub> to C<sub>6</sub> alkyl substituted cyclopentadienyl, indenyl, fluorenyl, or



"m" is 0 to 2, and each "n" is 1 to 4.

20. A method according to Claim 19 wherein said catalyst is selected from the group consisting of bis(2-pyridinoxy)titanium dichloride, (cyclopentadienyl)(2-pyridinoxy)titanium dichloride, and mixtures thereof.